Silole-core Dendrimers: A Facile Synthesis and Photophysical Properties

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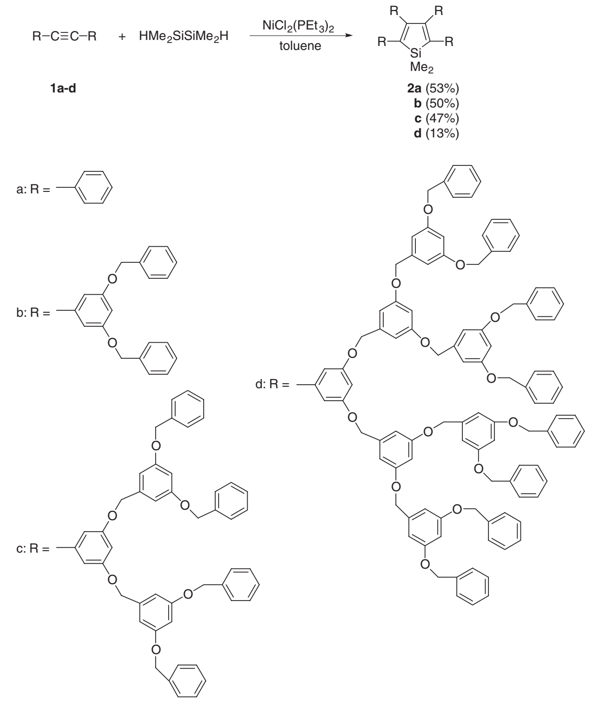
Silole-core dendrimers having benzyl ether-type dendron units, readily synthesized by the Ni-catalyzed reaction of benzyloxy-substituted diphenylacetylenes with 1,1,2,2-tetramethyldisilane, display, upon excitation of the dendron units, efficient energy transfer from the dendron units to the silole core, resulting in strong emission from the silole ring.

Siloles, silacyclopentadienes, have attracted great interest over the past decade because of their unique photophysical and electronic properties[1] and potential applications as organic electroluminescent (EL) devices.[2] The silole has a relatively low LUMO energy level due to the σ^*–π^* conjugation in comparison with a carbon analogue, cyclopentadiene. Recently, several reports have addressed synthesis of siloles with a variety of substituent groups[3] and silole-based polymers.[4] In view of the improvement of the photophysical properties, the aggregation leading to enhance the emission efficiency of a simple tetraphenylsilole was reported by Tang and co-workers.[5,6] The structural tuning of silole ring was also recently reported by Yamaguchi[7] and Pagenkopf.[8]

We designed silole-core dendrimers. Dendrimers are a class of highly ordered, three-dimensional, and tree-like macromolecules and potential building blocks for the construction of functional materials.[9] In this regard, dendritic macromolecules offer a special opportunity for improvement of photophysical properties, for example, a site-isolation of chromophores, a light-harvesting antenna, and an energy transfer interaction.[10] In the application to EL devices, it is also of interest to develop materials with improved stability and an alternative class of materials for solution processing. Recently, several groups have reported dendrimer-based EL devices.[11] We report herein a facile one-pot synthesis and photophysical properties of silole-core dendrimers.

Our synthetic strategy for the silole-core dendrimers is based on the nickel-catalyzed reaction of 1,1,2,2-tetramethyldisilane with disubstituted alkynes,[12] which has proven to work well for dendritic alkynes **1b**–**1d** affording silole-core dendrimers **2b**–**2d**. Thus alkynes **1b**–**1d**, prepared by the reaction of 1,2-bis(3,5-dihydroxyphenyl)acetylene with appropriate benzyl ether-type dendritic bromides,[13] were treated with the tetramethyldisilane in the presence of $NiCl_2(PEt_3)_2$ in refluxing toluene (Scheme 1). As the generation grows, the time required to complete the reaction increased and the reaction became less clean resulting in a lower yield, especially for **2d**. However, silole-core dendrimers **2b**–**2d** could be readily purified by column chromatography and the structures were characterized by FAB mass or MALDI-TOF mass spectrometry, GPC, and NMR spectroscopy.[14] This synthetic procedure demonstrates the alternative convergent approach via one-pot synthesis of the core for the construction of precise macromolecular structure.[15]



Scheme 1. Synthesis of silole-core dendrimers.

To the best of our knowledge, these are the first examples of silole-core dendrimers. The photophysical data in solution, along with those of the parent compound **2a**, are summarized in Table 1 and the absorption and fluorescence spectra of **2a**–**2d** are shown in Figure 1. In the absorption spectra, the silole-core dendrimers (**2b**–**2d**) have two absorption bands at about 280 and 360 nm, assignable to the benzyl ether-type dendrons and the focal silole ring, respectively. The intensity of absorption of the dendron units increased with increasing the generation of the dendrons, while the intensity and the position of absorption of the silole ring did not change significantly. When the silole ring was excited at 360 nm, the silole dendrimers **2b**–**2d** displayed an emission at about 500 nm. The fluorescence quantum yield (Φ_{FL}) increased with increasing the generation of the dendron units (Table 1). The Φ_{FL} of **2d** was about 200 times greater than that of the model compound **2a**, because the dendron units prevent the quenching processes for the silole ring effectively. Increased chromophore rigidity often leads to improved lumi-

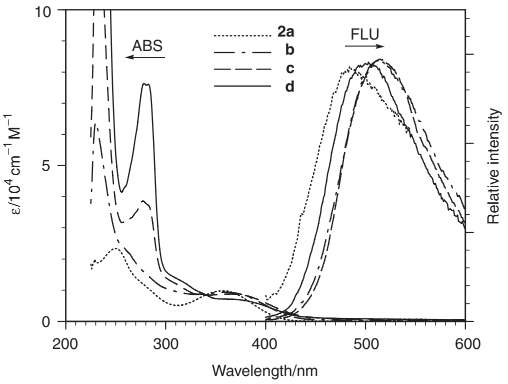


Figure 1. Absorption and fluorescence spectra of **2a**–**2d** in CH_2Cl_2.

Table 1. Photophysical properties of silole-core dendrimers **2a**–**2d**

Cmpd	Absorption		Fluorescence		
(Gn)	λ_{max}/nm	$\varepsilon/10^4\,cm^{-1}\,M^{-1}$	λ_{FLmax}/nm[a]	Φ_{FL}[b,c]	Φ_{ET}/%[d]
2a	249	2.34	485	5.0×10^{-4}	—[e]
(G0)	356	0.98			
2b	278[f]	1.59	514	2.5×10^{-2}	≈100
(G1)	360	0.93			
2c	277	3.85	514	6.8×10^{-2}	51
(G2)	366	0.88			
2d	278	7.64	503	0.12	28
(G3)	358	0.72			

[a]Excited at 360 nm. [b]Determined with quinine sulfate as a standard. [c]Fluorescence quantum yield, when excited at the core silole rings. [d]Energy transfer quantum efficiency from the dendron units to the core silole within the dendrimers, when excited at the dendron units (280 nm). [e]Not estimated. [f]Observed as a shoulder.

nescence by dually facilitating electron delocalization and minimizing vibrational–rotational events in the excited state. Interestingly, excitation of the benzyl ether-type dendron units at 280 nm also displayed an emission around 500 nm from the silole ring unit, but almost no emission from the benzyl ether-type dendron units was observed (310 nm),[9] indicating that the extensive energy transfer (ET) from the dendron units to the focal silole ring occurred within the dendrimers. The ET quantum efficiency (Φ_{ET}), estimated by a comparison of the absorption spectrum and the excitation spectrum of the silole-core dendrimers by monitoring the emission of the acceptor, i.e., the silole, are also listed in Table 1. The efficiency was essentially quantitative for **2b**. However, the energy transfer efficiency to the core decreased with the generation growth of the dendrons and dropped dramatically to 28% for **2d**.[16] The Förster-type ET is favored by a) the large spectral overlap between donor emission and acceptor absorption, b) the high molar absorption coefficient of the accepter, c) the high fluorescence quantum yield of the donor, and d) the short interchromophoric distance.[11] The present system was, however, not very high, especially for the higher generation,[9] probably because all of the requirements for the efficient Förster ET were not met. Further, the emission from the silole core observed upon excitation at the dendron units (280 nm) was more intense, approximately three times more for **2b** and **2c**, than that displayed by direct excitation of the silole core (360 nm). This "antenna effect" is the result of the larger extinction of the dendrimers at 280 nm compared to 360 nm.[9]

In conclusion, we have prepared the silole-core dendrimers by the nickel-catalyzed reaction of the tetramethyldisilane and dendritic acetylenes having poly(benzyl ether) units through the third generation. The findings herein reported would be important in view of optoelectronic applications. Further study along the line is currently in progress.

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16 When **2d** was excited at 280 nm, an emission around 390 nm was observed along with the emission at 500 nm from the silole ring. A detailed photophysical property of the dendrimers needs further study.

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